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THERMAL ANALYSIS OF REACTIVITY OF PYROPHORIC
FUELS IN A CHEMICALLY SECURE ENVIRONMENT

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SUMMARY

Investigations into the modes and rates of reaction of pyrophoric solids with potential use as fuels in decoy flares are particularly difficult to conduct when it is desired to study a variety of atmospheric and temperature conditions. Sample integrity prior to exposure to a given reaction environment is also difficult to guarantee. Control of reaction rate by exposure to diluted atmospheres is also a problem.

This report provides details on a technique wherein sample preparation, handling, and exposure to a reactive environment are all completed within a secure environment. The overall system involves thermogravimetric analysis of materials in an inert atmosphere enclosure. The samples can be studied under a variety of atmospheric, changing atmospheric, and temperature conditions, with static or flowing environments with adjustable flow rates. The procedures are rapid and efficient and provide reasonable turnaround times, and they guarantee quantitative analytical information on mass change and temperature effects during the actual reaction period. Further, calorimetric data and heats of reaction under a variety of reaction conditions, and differential thermal analytic data may be easily obtained as well. Finally, the reaction products are then available for subsequent analysis for surface effects, ratios of products, etc.

The basic procedure is to effect sample preparation or synthesis in an inert atmosphere environment, transfer a measurable quantity of sample to a given thermoanalytic apparatus inside the inert atmosphere enclosure, and proceed with setting up of experimental conditions. Then the desired reactive atmosphere is introduced to an isolated sample compartment, the quantitative data gathered, and the sample compartment purged prior to recovery of the products and loading of a new sample. The procedure is quick, reliable, and completely reproducible.

PREFACE* (U)

(U) This report of NAVAIR-sponsored research consists entirely of work done at the Naval Weapons Support Center (NAVWPNSUPPCEN), Crane, and was supported by funds from AIR-32R.

* In order to specify procedures adequately, it has been necessary to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the Navy, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

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Background

Pyrophoric solids present particular difficulties for handling when it is desired to prepare, purify, and study their properties in a variety of ways. Their air-reactivity requires an inert atmosphere such as dry nitrogen or argon to be used during all manipulations. Thus, so-called dry-lab enclosures are used for their study. In situations where it is desirable to study the actual behavior of such materials in reactive environments, new problems quickly arise.

When pyrophoric materials are removed from a secure environment to the ambient world in order to perform experiments, there is a significant danger of sample contamination and degradation during all transfer operations. Then the sample integrity at the time of a test procedure is always in doubt. If, on the other hand, the reactive environment is taken to the sample and if contamination of the secure environment can be prevented, then a more reliable experimental situation prevails. Of course, there may still be difficulties associated with modifications in the reactive environment during experiments. Nevertheless, controlled, reproducible, reactive situations are desirable when it is necessary to characterize the reactive behavior of a pyrophoric material which has potential use in flare devices.

We have utilized an approach involving performance of the reaction studies in a dry-lab facility such that sample integrity is maintained prior to a reaction situation. During the actual experimental runs, the dry-lab atmosphere is secure, such that sample preparation is not threatened. Thus, samples for study can be prepared, stored, and run simultaneously in a secure environment, reproducibly, without concern for the sample integrity or for contamination of the enclosure atmosphere.

Experimental

The work to be discussed will be confined to thermogravimetric analysis (TGA) in which the mass and temperature changes in pyrophoric sample materials were observed as functions of time, when reactive gas atmospheres were introduced to the sample environment. The entire system is shown schematically in Figure 1. A Du Pont Model 951 TGA balance was used for these studies and was placed in a Vacuum Atmospheres Inert Atmosphere Enclosure which was routinely operated with an argon atmosphere, which contained less than 0.3 ppm O_2 and H_2O , and less than 3 ppm N_2 . The TGA balance was connected to a Du Pont Model 990 Thermal Analysis console outside the enclosure, and all the operating conditions were controlled from the console. The mass balance was set up so that a gas flow could be maintained through the apparatus. Then a gas proportioner was used to allow rapid switchover from one sample atmosphere to another, as well as to allow mixing of two gases in any proportions. For example, a mixture of 20% O_2 in Ar could be used to simulate Air without N_2 to eliminate potential reaction conflicts with nitrogen.

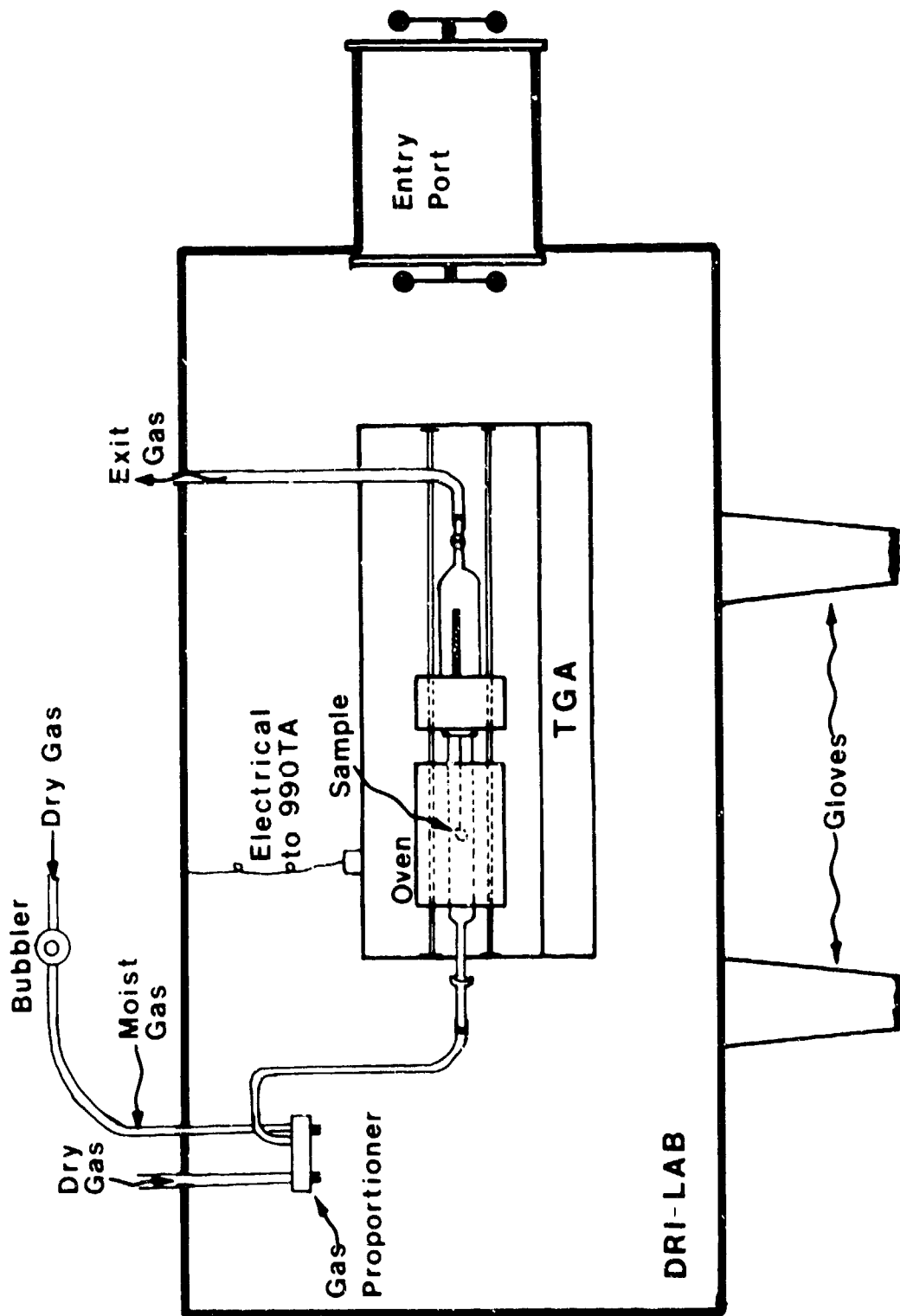


FIGURE 1. Diagram of Thermogravimetric Analysis Setup in the Dri-Lab

The sample materials to be discussed were pyrophoric: Lithium metal powder (-140 mesh) and lithium-boron alloy, Li_7B_6 (-50 mesh). Sample quantities were routinely 5-10 mg in size and were placed in a platinum pan suspended from a quartz balance arm. The loaded balance was allowed to reach equilibrium, under a flow of dry argon at about $15 \text{ ml} \cdot \text{min}^{-1}$, at the desired reaction temperature. Then the reactive gas atmosphere was introduced into the apparatus, flowing also at $15 \text{ ml} \cdot \text{min}^{-1}$, and mass and temperature changes with time were monitored. Typical run times were 3-4 hours, although some were much longer. The experimental arrangement also allowed the introduction of moisture into the gas flow, so that the effects of humidity on reactive atmospheres could be studied, and moisture alone in an inert gas stream could be examined.

The gases used as "dry" were Matheson Purity Air, Oxygen, Nitrogen, and Argon, with moisture contents less than 5 ppm, and the Air was CO_2 free as well. Gases used during humidity studies were just High Purity grade.

Results and Discussion

In a typical procedure, the TGA balance would be under dry Ar at the start of a run. The empty Pt pan was first tared to zero mass at the desired reaction temperature and gas flow rate. Then the balance compartment was loaded with a sample and a period of time allowed for the balance to equilibrate in the dry Ar stream. Next, the sample atmosphere was changed to the desired reactive gas. Usually, a period of 3-5 minutes was required to establish a reactive atmosphere before any indication of mass change was observed.

In Figure 2 are the data from reaction of Li metal with dry O_2 and Air, at 190°C , above the Li fusion temperature. In both gases, the reaction process occurs readily, and the data are very similar. This similarity means that Li_2O is the product from dry Air, and, therefore, that Li_3N formation is not a significant competing reaction. The slight differences in the data can be attributed to differences in gas flow rates and O_2 concentration. The significant information is the similarity in results from two experiments using different gases. The fact that the sample handling is accomplished in a secure environment allows us to infer product and reaction similarities without having to be concerned about a possible role of catalytic contaminant picked up during transfer operations of such air- and moisture-sensitive materials.

In Figure 3 are the data from three experimental runs on the reaction of Li metal powder with humid Ar. The only reactive material in such a gas flow is moisture, and the predicted final product is $\text{LiOH} \cdot \text{H}_2\text{O}$. The data clearly show this product formation, along with an earlier inflection in the curves corresponding to initial formation of LiOH . Further, the data show that when the atmosphere over the sample was changed back to dry Ar, the water of hydration was quickly lost, with the product returning to LiOH . The observed mass changes correspond to:

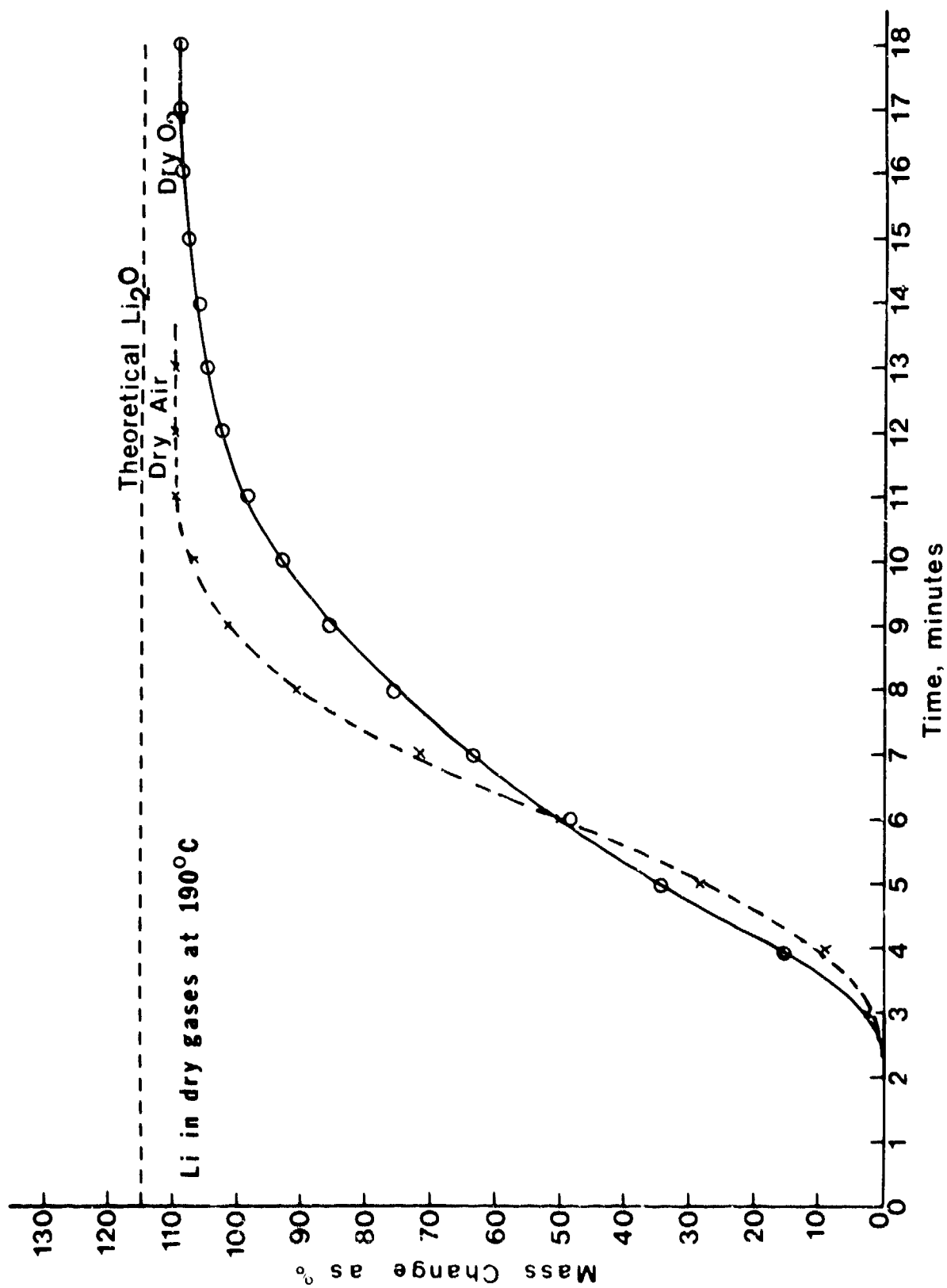


FIGURE 2. Reactivity of Lithium Metal with an Atmosphere of Dry Air at 175°C . Percent Mass Change vs. Time.

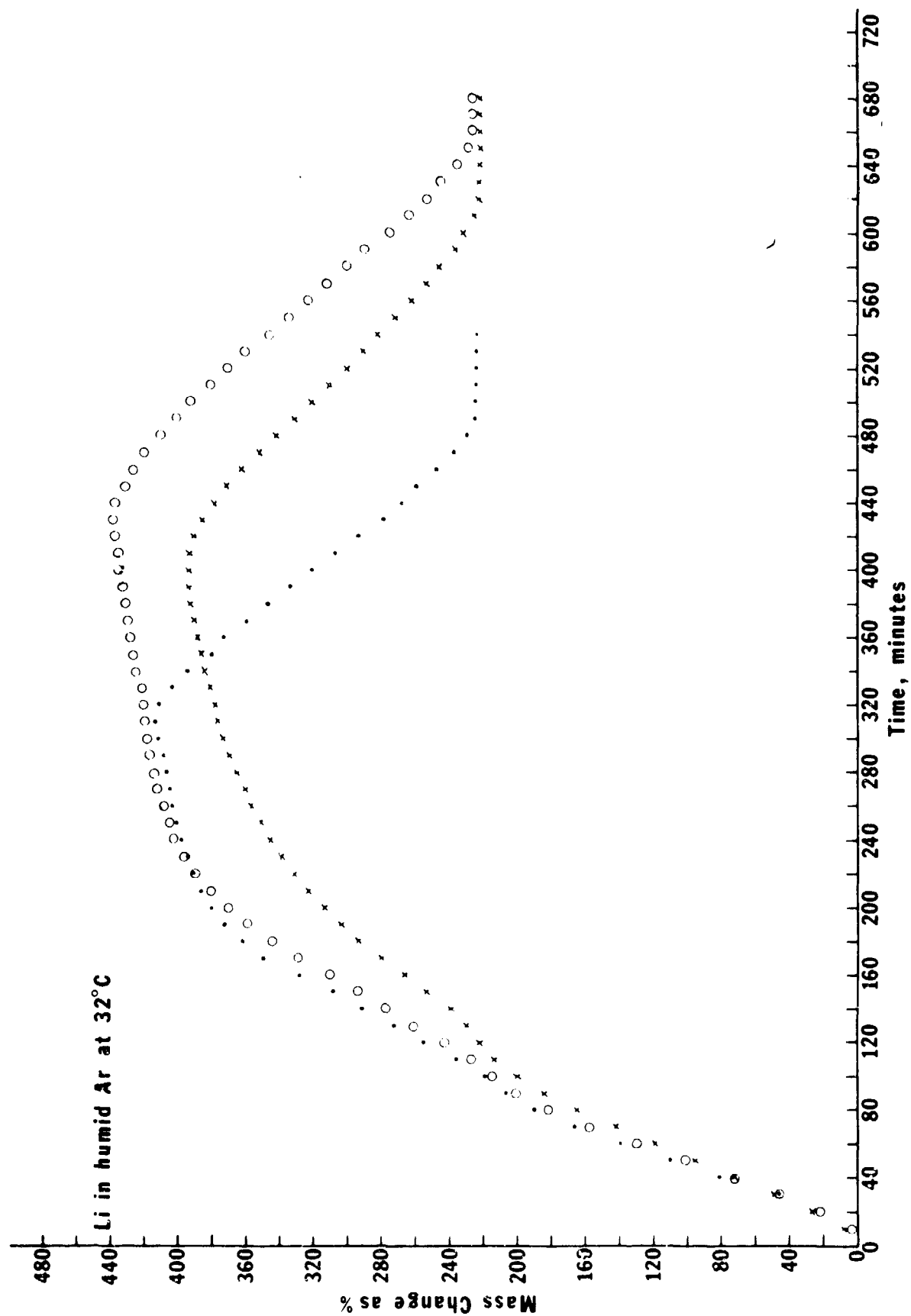
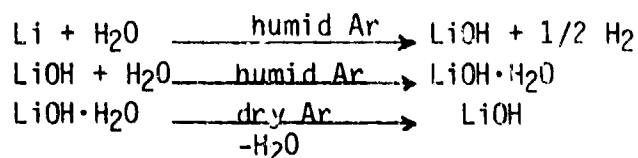


FIGURE 3. Reactivity of Lithium Metal with Moist Ar, Triplicate Run. Percent Mass Change vs. Time.



and all of this occurs readily at ambient temperature (32°C). Finally, the three runs indicate the reproducibility of the reaction processes. Thus, there is freedom from concern about sample contamination. The processes which lead to changes in sample mass must be a consequence of only the components of the atmosphere over the sample. The confidence about this fact leads in a natural way to the conclusions drawn from the data in the next two figures.

In Figure 4 are presented the data from reactions of Li metal and Li₇B₆ alloy with humid Ar and N₂, at ambient temperatures. These data allow two sets of comparisons to be made. First, it has been reported that Li₃N formation occurs readily from moisture catalyzed reaction with N₂ gas. Second, we wish to know the comparative reactivity of Li and Li₇B₆ in similar atmospheres. With regard to the first, using the data from reaction of Li metal, it seems evident that the reaction process in both atmospheres is the one outlined above in the equations. Thus, the process is formation of LiOH, conversion to LiOH·H₂O, and subsequent dehydration to LiOH in the dry Ar stream. Li₃N does not appear to form.

Next, we address the second question about the comparative reactive behavior of the two Li materials in the respective atmospheres. The data, which are in percent mass change for Li in both materials, clearly show the similarities in the behavior of the two materials. This allows us to say that Li₇B₆ behaves essentially like Li metal, that the Li component of the alloy is the reactive portion, and that its behavior at ambient temperature has been modified only slightly by incorporation into the alloy. This modification amounts to a slight reduction in overall reactivity.

Then, in Figure 5, we examine the data for the same two materials in humid Air and O₂, at ambient temperature. These data once again show that the preponderant and probably the only significant reaction is with water vapor. Lithium is simply not reactive toward O₂ or N₂ in humid environments at ambient temperatures. Also, as a consequence of the preferred reactions with H₂O, Li in both materials behaves essentially identically.

Conclusions

We have been able to investigate the reactivity of two chemically related pyrophoric materials with a variety of atmospheres and to draw conclusions about pathways and relative reactivities without concern about confusion of the data with unwanted catalytic contamination of the samples. This was achieved through the use of a secure environment in which all stages of sample preparation and study are reliable and reproducible. Thus, we can arrive at a significant understanding of the reaction processes for materials which are inherently difficult to handle, in a straightforward fashion. This understanding can then be transferred to the behavior of these materials when they are exposed to an ambient environment as they are used as fuels in flare devices.

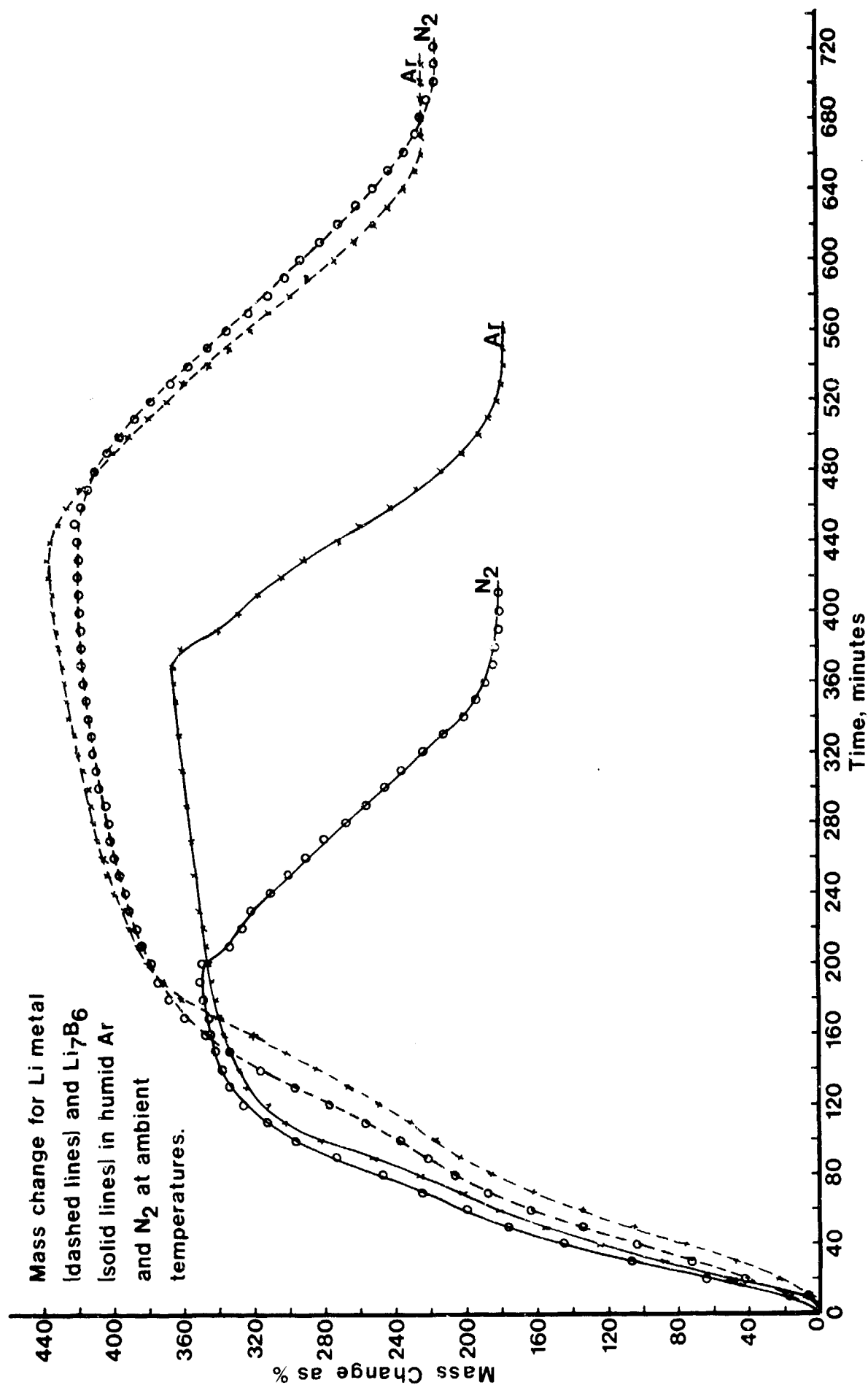


FIGURE 4. Reactivity of Lithium Metal and Li_7B_6 Alloy with Atmospheres of Moist Ar or N_2 at Ambient Temperatures.
Percent Mass Change vs. Time.

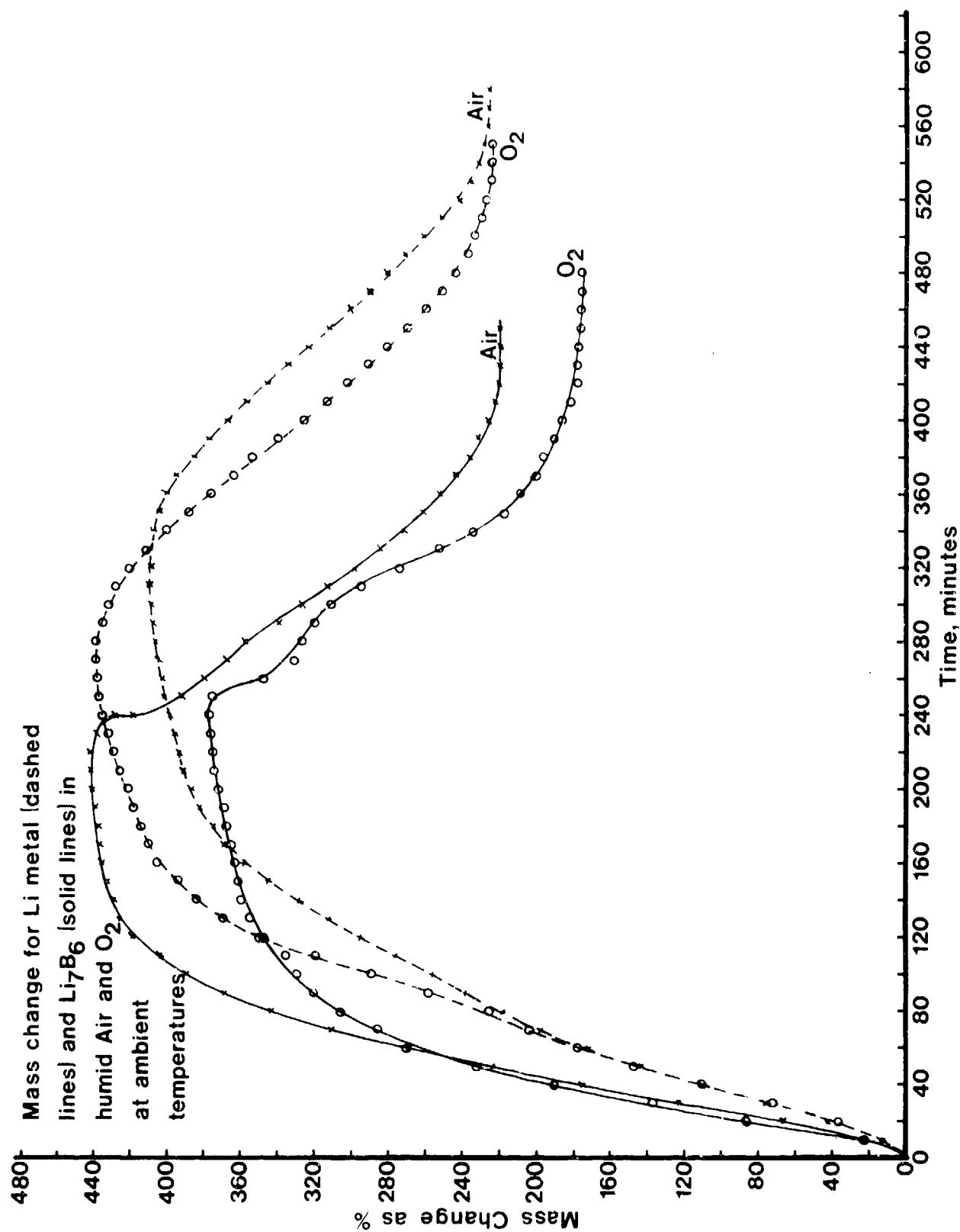


FIGURE 5. Reactivity of Lithium Metal and Li_7B_6 Alloy with Atmospheres of Moist Air or O_2 at Ambient Temperatures. Percent Mass Change vs. Time.

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